# Thermopower peak in phase transition region of (1-x)$La_{2/3}Ca_{1/3}MnO_3$/xYSZ

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The thermoelectric power (TEP) and the electrical resistivity of the intergranular magnetoresistance (IGMR) composite, (1-x)$La_{2/3}Ca_{1/3}MnO_3$/xYSZ ( LCMO/YSZ ) with x = 0, 0.75%, 1.25%, 4.5%, 13% 15% and 80% of the yttria-stabalized zirconia (YSZ), have been measured from 300 K down to 77 K. Pronounced TEP peak appears during the phase transition for the samples of x > 0, while not observed for x = 0. We suggest that this is due to the magnetic structure variation induced by the lattice strain which is resulting from the LCMO/YSZ boundary layers. The transition width in temperature derived from $d\chi/dT$, with $\chi$ being the AC magnetic susceptibility, supports this interpretation.

## I. INTRODUCTION

The colossal magnetoresistance (CMR) material has been one of the focused points in the research community due to its promising potential in the applications and its complicated properties in the basic physics research. Many models have been proposed in the early days to discuss the observed phenomena, from the double exchange model[1–4] for the ferromagnetic phase at low temperature (LT-FM phase) to the bi-polaron model[5,6] for the paramagnetic phase at high temperature (HT-PM phase). However, none of these alone can satisfactorily explain the complicated behaviors occurring during the Metal/Insulator (MI) or the Ferromagnetic/Paramagnetic (FM/PM) phase transition. Deeper understanding into the physics of the CMR phase transition is therefore necessary. Among the existing models, the percolation theory of the FM/PM coexistence in the phase transition has received much attention with many supporting evidences[7–9].

In some of the previous reports for the TEP measurements on the manganites, a pronounced positive peak or an abrupt jump has been observed during the phase transition[10–12]. However, there have been other reports on the samples of the same compositions without exhibiting any peak or jump in the TEP during the phase transition[13,14]. In one of our previous experiments[15], the $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ samples with x = 0, 0.05, 0.15, 0.20 have been studied. There is a TEP peak showing up during the phase transition for the high doping sample, x = 0.2, while not observed for the other low doping ones. An intermediate phase resulting from the magnetic structural inhomogeneity induced by the lattice mismatch, which is a direct result of the random distribution of different Perovskites A-site cations, has been proposed to explain this phenomenon. By the similar mechanism, any defect-induced mismatch or the strain propagated from the interface layers in the lattice would introduce similar effect on the magnetic structure. Hence a TEP jump would appear during the phase transition. This behavior in TEP have been observed in the thin film sample of single crystal $La_{2/3}Ca_{1/3}MnO_3$[10,11], and in the samples of $La_{0.7}Ca_{0.3}MnO_3$ by different heat treatment in the oxygen environment[16]. The underlying cause for the TEP peaks to occur is perhaps other than an intrinsic one as suggested with the charge-orbit coupling[17] or the band narrowing[12] effects. Instead, the lattice mismatch caused by the strain resulting from the substrate for the former case and from the deficiency of the oxygen for the latter one would, perhaps, provide a consistent picture for the understanding.

In order to gain deeper insights into the properties of the CMR manganites, especially during the phase transition, we have carried out extensive measurements on the series of the samples, the (1-x)$La_{2/3}Ca_{1/3}MnO_3$/xYSZ compound with x = 0, 0.75%, 1.25%, 4.5%, 13%, 15%, and 80%. These include the temperature dependent resistivity ($\rho - T$), the TEP, and the AC susceptibility measurements. The correlation of the TEP peak with the YSZ composite ratio, x, has been studied. The lattice strain induced by the boundary layers of the YSZ insulator intermixed with the LCMO phase provides a satisfactory basis for the understanding of the TEP peak to appear during the phase transition. In addition, the structure effect of the two-component composite on the electrical transport properties and the phase transition temperature $T_C$ has been explained within the framework of the percolation theory.

## II. SAMPLE PREPARATION

The LCMO/YSZ samples were fabricated by double-staged production procedure as reported previously[18]. Nanometric powders of the LCMO was first prepared by the sol-gel method and then sintered at 1300 $^oC$ for 10 hours to obtain powdered crystals of grain size $\sim 20$ $\mu$m. Then, it was mixed thoroughly with the YSZ powders

of grain size $\sim 2$ $\mu$m for the heat treatment in the ambient air environment at 1350 $^oC$ for another 10 hours. The crystal structure was then characterized by the X-ray diffraction (XRD) analysis using the Cu $K_\alpha$ source. The YSZ phase is identified for the samples of x $> 5\%$, and the lattice parameters of the LCMO phase remain unchanged within the level of 0.001 $\mathring{A}$ for all of the samples. This evidence indicates that the LCMO and the YSZ phases exist independently to form solid intermixture, without the inter-diffusion of the ions from the YSZ phase into the LCMO phase during the heat treatment. The results by the SEM images provide further evidence that the YSZ phase exists separately from that of the LCMO[18].

## III. EXPERIMENT

The zero-field temperature dependent resistivity ($\rho - T$) measurements have been carried out by the standard 4-probe method. Typical $\rho - T$ curves of the CMR materials are obtained and presented in Fig. 1 for all of the samples except for the one of x = 80%, which has the insulator property with the resistance $> 10^{12}\,\Omega$. The temperature and the resistivity of the MI transition peak have been plotted against the mixing ratio, x, in the inset of Fig. 1. The zero-field $\rho - T$ property from the present work is consistent with the result reported in the previous experiment[18]. The lowest transition temperature occurs at $x_m = 4.5\%$ with the corresponding peak resistivity having the largest value, see the inset of Fig. 1. At the low mixing ratio with x $< x_m$, the distribution of the YSZ forms insulation layers encompassing the LCMO clusters completely. This has been confirmed by the direct SEM observation. At this structure, the mechanism of the electrical conductance between the LCMO phase separated by the YSZ phase is realized by the tunnelling conduction through the insulating YSZ layer. With the x increasing from 0 to $x_m$, the size of the LCMO cluster decreases with the inter-granular effect going up[18]. Accordingly, the peak resistivity, $\rho_{peak}$, increases and the peak temperature, $T_\rho$, goes down, at the increasing x, see the inset of Fig. 1. On the other hand, for the high x samples at x $> x_m$, the insulating YSZ phase tends to form cluster-like structure and the LCMO phase would constitute a 3-dimensional percolation connection without being surrounded completely by the YSZ phase. This makes the conduction behavior of the high x samples tends to resemble the one of x = 0 at the LT-FM phase. For the sample of x = 80 %, which exceeds the threshold density by the percolation theory, the conducting passage is disconnected within the sample by the YSZ insulator and the insulation state is resulted.

The temperature dependent TEP measurement ($S - T$ measurement) has been conducted by the differential DC method from 320 K down to 77 K. The results are shown in Fig. 2. For the particular sample of x = 0, which is $La_{2/3}Ca_{1/3}MnO_3$, the TEP shows a smooth transition from the low temperature metallic behavior to the high temperature $1/T$ diffusive behavior. With the mixing of the YSZ component into the LCMO phase, the composite compound, LCMO/YSZ, exhibits the usual metal-like TEP behavior in the LT-FM phase and the usual semiconductor-like property, *i.e.*, the $1/T$ dependence, in the HT-PM phase. However, in high contrast to the result for the sample of x = 0, an abrupt jump appears in the TEP during the phase transition for all of the samples with x $> 0$ except for the one of x = 80%. It is difficult to make a reasonable measurement of the TEP for x = 80% because of its insulation property. The above results from the TEP measurements imply that the appearance of the jump is associated with the existence of the boundary layer between the YSZ phase intermixed with the LCMO phase, since it appears even for the composite ratio as little as x = 0.75 %, considering that the YSZ phase is insulating by itself without an experimentally-determined TEP value and the LCMO phase alone exhibits smooth transition during the phase transition.

By the fact that the electrical measurement does not have the corresponding abrupt change during the phase transition, the TEP actually reveals more subtle variation of the phase transition. Considering the materials consisting of multiple components with different electrical conductivity, the TEP reflects the contributions from the separate composing ingredients weighted by the corresponding conductivity. For the LCMO/YSZ material at x $> x_m$, unlike the electrical conductance which reflects predominantly the conducting property of the components with high conductivity, the TEP has a non-negligible or sometimes very large contribution from the poor conducting parts of the sample because of the fact that materials of poor conductivity usually have higher TEP value. At x $< x_m$, the resistivity of the LCMO phase enclosed by the YSZ layer mainly reflects the intergranular effect. However, for the TEP, phonon motion is the major factor to affect the electron movement. The temperature drop across every composition of the sample is homogeneous. Hence, it is more sensitive to the property variation occurring in the boundary layer. In Fig. 3, the peak temperatures of the MI transition, $T_\rho$, and the TEP maxima, $T_S$, are plotted against x. The effect of the YSZ composition on these two characteristic temperatures are similar with the minimum temperatures occurring at $x_m = 4.5$ %. However, the variation amplitude of $T_S$ is much less than that of $T_\rho$. Since the electrical conductance is affected mainly by the high conducting composition of the sample and the TEP, which is the transport property of zero current, reflects the overall property of the sample. Therefore, the TEP has smaller x dependence than the electrical conductivity does.

Similar positive jump has been observed on the Yttrium-doped manganites, $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$ in the previous experiment[15] and has been interpreted as

due to the magnetic structural inhomogeneity caused by the doping-induced lattice mismatch. Hence, it is reasonable to infer that the positive jump occurring under the current investigation for the LCMO/YSZ samples is caused by the magnetic inhomogeneity resulting from the lattice mismatch, which is induced by the strain from the boundary layer of the YSZ and the LCMO phases. The lattice variation would modify the coupling strength between the adjacent magnetic moments and result in the inhomogeneous distributions of the PM/FM magnetic phases in the surrounding regions of the boundary layers.

The magnetic transition is studied by the AC magnetic susceptibility measurements. The applied AC field for the measurements is 10 Oe at 133 Hz with a background field close to zero. Temperature range for the measurements is from 300 K down to 10 K. The transition for all of the samples appears to be smooth. One can determine the magnetic transition width in temperature, $\Delta T$, by calculating $\mathrm{d}\chi/\mathrm{d}T$. For a ferromagnetic transition, $\mathrm{d}\chi/\mathrm{d}T$ shows a peak at the transition temperature $T_C$ with the width characterizing the transition sharpness. A sharp transition in temperature is obtained for the sample of x = 0 while a much wider transition, at least twice that of the x = 0, for the rest ones. This indicates that the effect of the magnetic inhomogeneity induced by the strain of the boundary layer is non-negligible. In Fig.4, the TEP peak value, $S_{peak}$, and the magnetic transition width in temperature, $\Delta T$, are plotted against x. Similar x-dependence of these two quantities revealed in the figure further supports our conjecture that the abrupt jump in the TEP measurement is strongly correlated with the magnetic inhomogeneity caused by the boundary strain.

In some of the previous experiments, magneto-thermoelectric effect has been performed on the $La_{0.67}Ca_{0.33}MnO_3$ thin film,[10,11]. Two implications are obtained in consistent with the explanations for our experiment. First of all, the TEP peak appears in the thin film sample of single crystal LCMO phase without any doping or intermixing effect. This is different from the TEP behavior of the pure LCMO sample, x = 0, observed in the current experiment. However, if one takes into account the strain effect of the boundary layer adjacent to the substrate for the thin film sample, the underlying cause for the TEP peak would be the same as in our experiment. The second implication is that the cause for the TEP peak is magnetic, since the applied field would suppress the magnitude of the peak and display the magneto-thermoelectric effect.

## IV. CONCLUSION

For the (1-x)$\mathrm{La_{2/3}Ca_{1/3}MnO_3}$/xYSZ compound, the existence of the YSZ insulator introduces two major effects into the original pure LCMO materials. First of all, this is to produce artificially the two-component co-existence structure for the investigation of the electrical conductance within the LCMO phase. The conductance changes from the tunnelling region at low x, with the thin layer of YSZ insulator encompassing the LCMO phase, to the percolation conductance region at high x, in which the YSZ forms cluster-like structure with the LCMO phase existing in percolation-typed connection. The peak temperature, $T_\rho$, in the $\rho - T$ measurement, has a minimum at x = 4.5 %, with the corresponding resistivity value, $\rho_{peak}$, reaching the maximum, inset of Fig. 1. This corresponds to the cross-over region from the tunnelling to the percolation-typed conductance. The temperature of the peak in the TEP measurement, $T_S$, has a similar x-dependence as the MI transition, but with a much smaller variation range as shown in Fig. 3. This is owing to the fact it is a zero current transport property. The poor conducting part of the sample, though contributes much less in the electrical conductance, has an important contribution to the TEP behavior. Secondly, the existence of the YSZ composition introduces boundary layer into the LCMO phase. The appearance of the TEP peak depends crucially on the existence of the YSZ composition. It takes the YSZ ratio as little as x = 0.75% to induce large TEP peak, see Fig. 2. This indicates that the underlying cause for the TEP peak to occur is on the boundary layer rather than on the bulk YSZ composition. One of the plausible conjectures is that the strain in the boundary layer would modify the coupling strength of the magnetic moments within the layer and affect the conduction property due to the inhomogeneity of the magnetic composition. From the x dependence of the magnetic transition width in temperature, $\Delta T$, determined by $d\chi/dT$, see Fig.4, it shows that the transition width is highly enlarged in accordance with the existence of the YSZ phase. For the sample of x = 0, on the other hand, the transition is much sharper. This indicates that the boundary layer plays an important role on the magnetic structure along with the TEP behavior during the CMR phase transition. From the magneto-thermoelectric effect performed on the $\mathrm{La_{0.67}Ca_{0.33}MnO_3}$ thin film in the previous experiments[10,11], one can reach the conclusion that the TEP peak is induced by the lattice strain in the boundary layer of the LCMO phase and is magnetic in origin.

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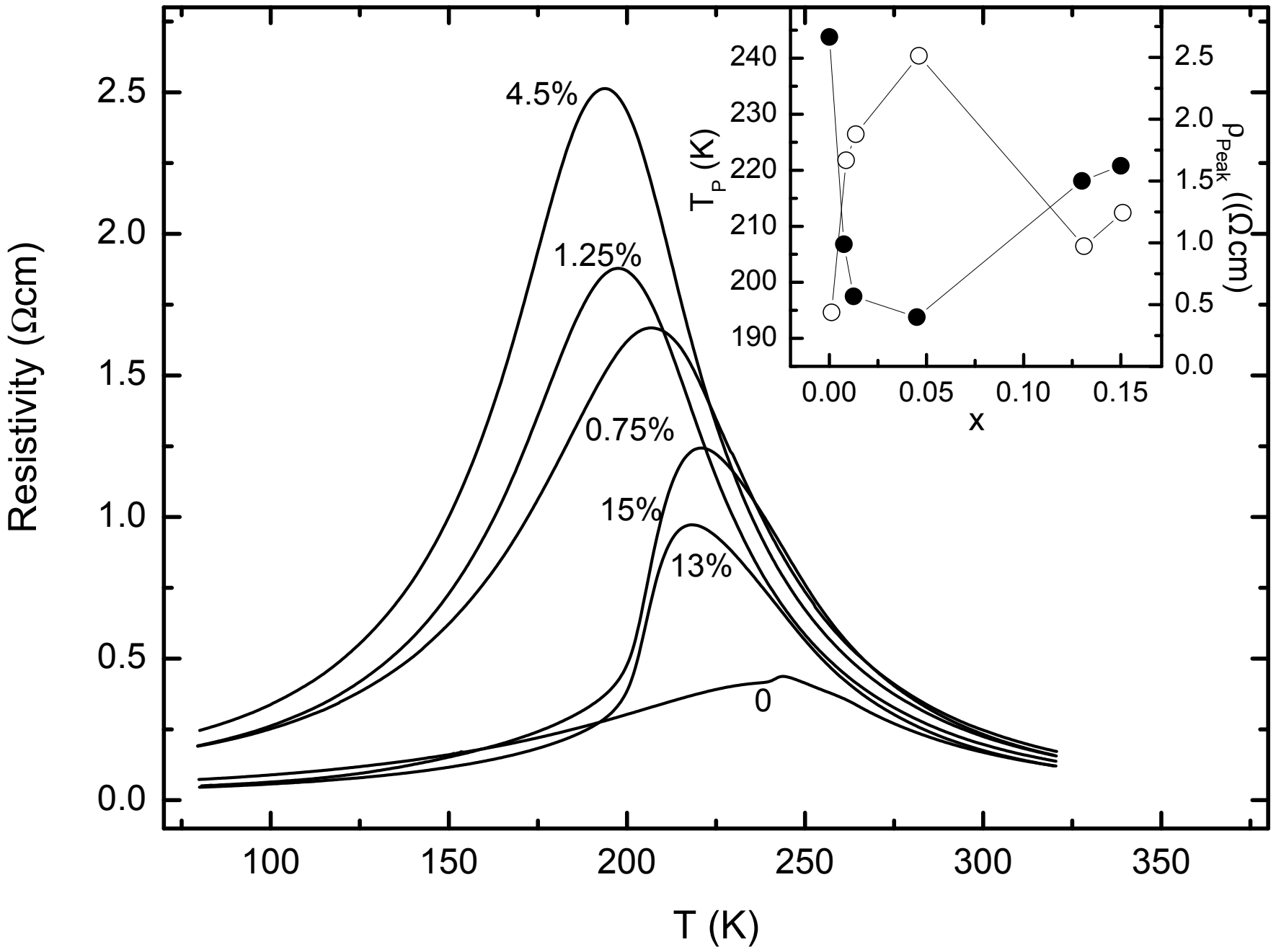
[1] C. Zener, Phys. Rev. **82**, 403 (1951)
[2] P. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955)
[3] J. B. Goodenough, Phys. Rev. **100**, 564 (1955)
[4] P. G. de Gennes, Phys. Rev. **118**, 141 (1960)
[5] A. S. Alexandrov and A. M. Bratkovsky, Phys. Rev. Lett. **82**, 141 (1999)
[6] A. S. Alexandrov and A. M. Bratkovsky, J. Phys.: Condens. Matter **11**, 1989 (1999)
[7] P. J. M. Bastiaansen and H. J. F. Knops, J. Phys. Chem. Soids **59**, 297 (1998)
[8] M. Fash, S. Freisem, A. A. Menovsky, Y. Tomioka, J. Aarts, and J. A. Mydosh, Science **285**, 1540 (1999)
[9] R. D. Merithew M. B. Weissman, F. M. Hess, P. Spradling, E. R. Nowak, J. O'Donnell, J. N. Eckstein, Y. Tokura, and Y. Tomioka, Phys. Rev. Lett. **84**, 3442 (2000)
[10] M. Rubinstein, R. E. Treece, J. S. Horwitz, and D. B. Chrisey, Appl. Phys. Lett. **68**, 1576 (1996)
[11] M. Jaime, P. Lin, S. H. Chun, and M. B. Salamon, Phys. Rev. B **60**, 1028 (1999)
[12] J. Fontcuberta, A. Seffar, X. Granados, J. L. García-Muñoz, X. Obradors and S. Piñol, Appl. Phys. Lett. **68**, 2288 (1996)
[13] M. F. Hundley and J. J. Neumeier, Phys. Rev. B **55**, 11511 (1997)
[14] P. Mandal, Phys. Rev. B **61**, 14675 (2000)
[15] W. Liu, C. P. Chen, W. Guan, S. S. Yan, Z. C. Xia, and S. Liu, manuscript in preparation.
[16] R. Mahendiran, S. K. Tiwary, and A. K. Raychaudhuri, Phys. Rev. B **54**, R9604 (1996)
[17] S. Nakamae, D. Colson, A. Forget, I. Legros, J.-F. Marucco, C. Ayache, and M. Ocio, Phys. Rev. B **63**, 092407 (2001)
[18] S. L. Yuan, Z. C. Xia, S. Liu, Z. Y. Li, G. Peng, J. Tang, G. H. Zhang, L. J. Zhang, W. Feng, and C. S. Xiong, Chin. Phys. Lett. **19**, 1168 (2002)

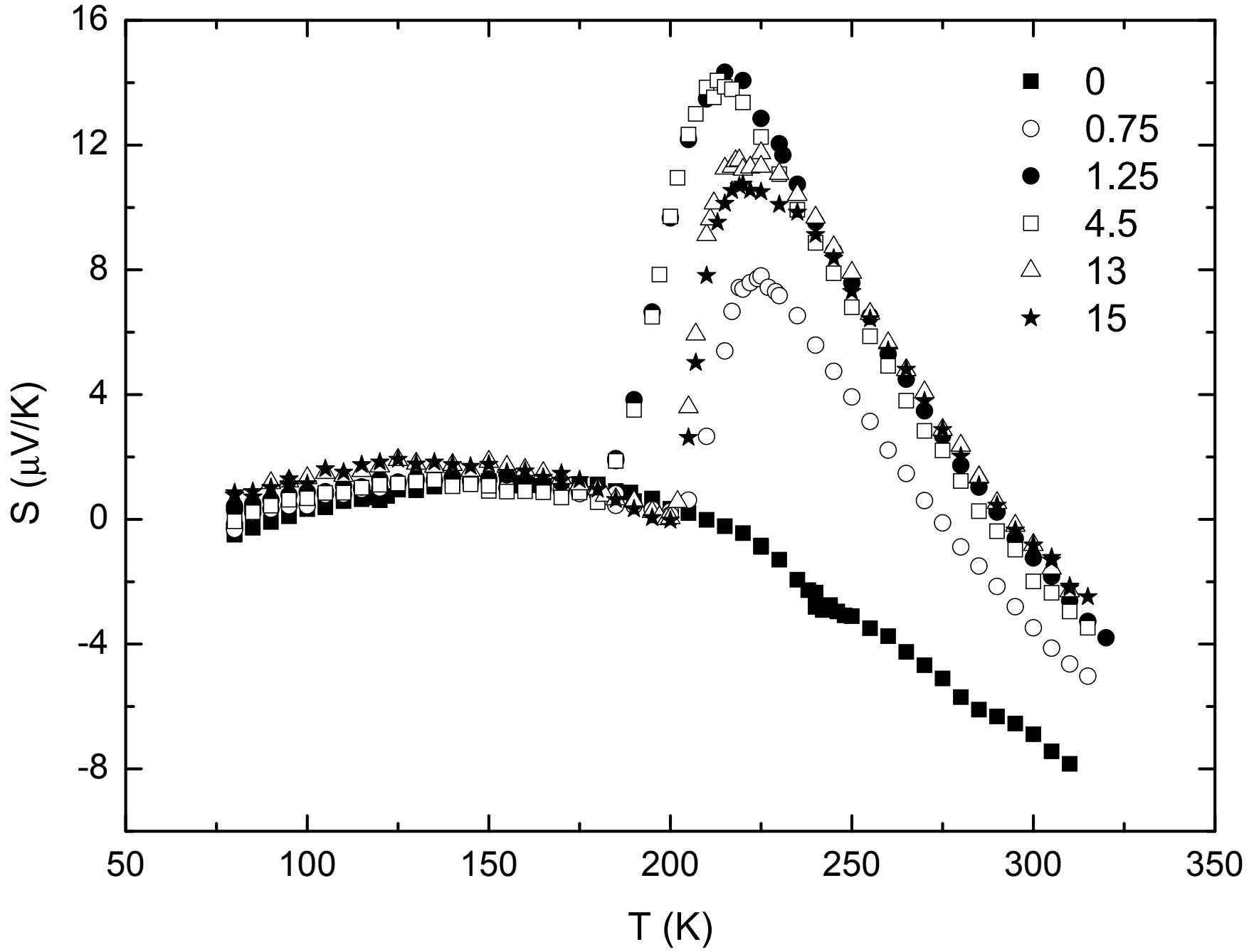
FIG. 1. The $\rho - T$ curves for the LCMO/YSZ samples with x = 0, 0.75%, 1.25%, 4.5%, 13%, and 15%. The inset presents the x dependence of the peak temperature, $T_P$, and the resistivity of the peak, $\rho_{peak}$, in the $\rho - T$ measurements.

FIG. 2. The temperature dependence of TEP from 77 K to 320 K for the samples of x = 0, 0.75%, 1.25%, 4.5%, 13%, and 15%. The sample of x = 0 is the pure LCMO polycrystalline.

FIG. 3. The x dependence of the peak temperatures, $T_P$, in the $\rho - T$ measurement and, $T_S$, in the TEP measurement.

FIG. 4. The x dependence of the TEP peak value, $S_{peak}$, and the magnetic transition width in temperature, $\Delta T$.


Resistivity (Ωcm)
T (K)
4.5%
1.25%
0.75%
15%
13%
0
$T_P$ (K)
$\rho_{Peak}$ (Ωcm)
x


16
12
8
4
0
-4
-8
S (μV/K)
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100
150
200
250
300
350
T (K)
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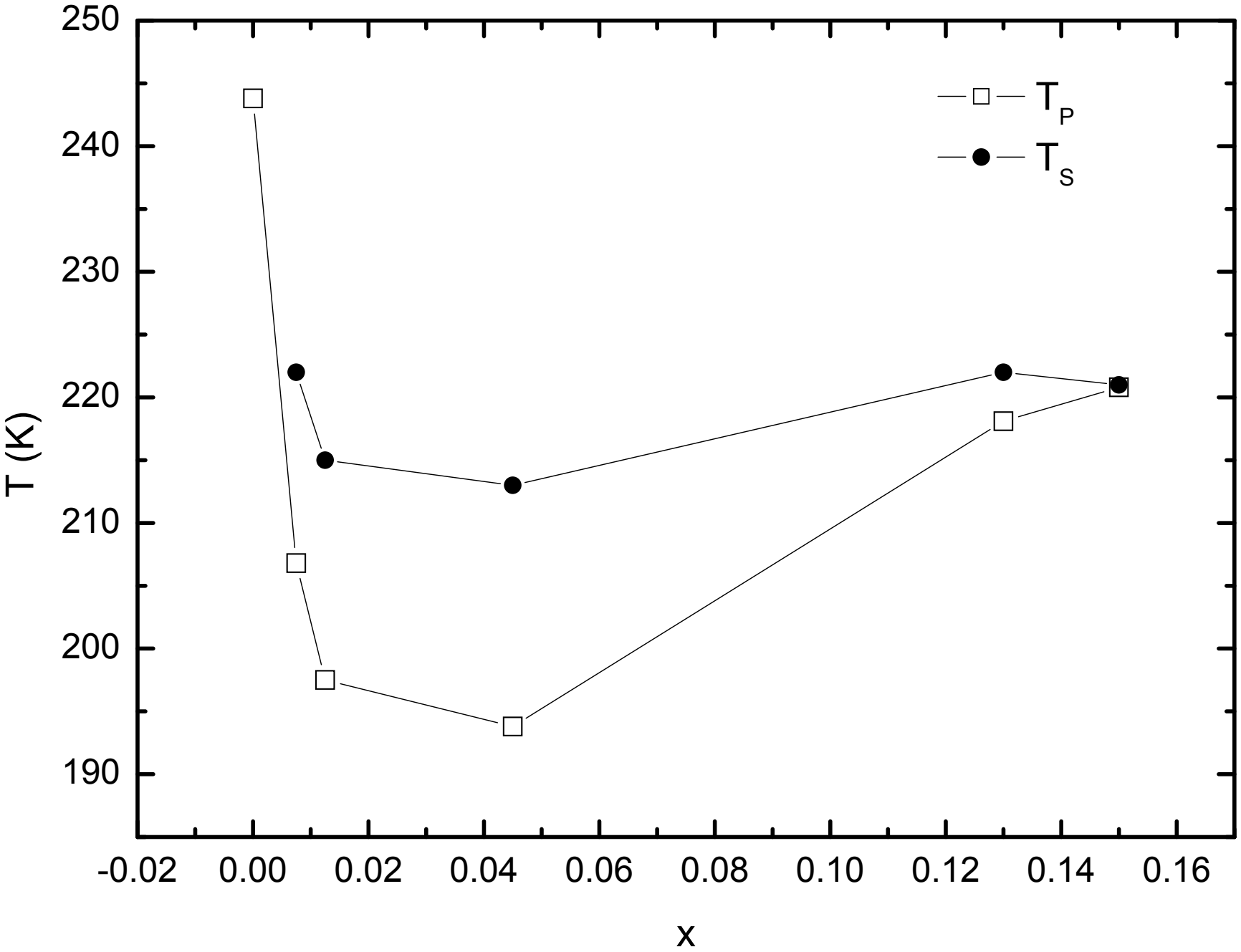
0.75
1.25
4.5
13
15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240
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190
T (K)
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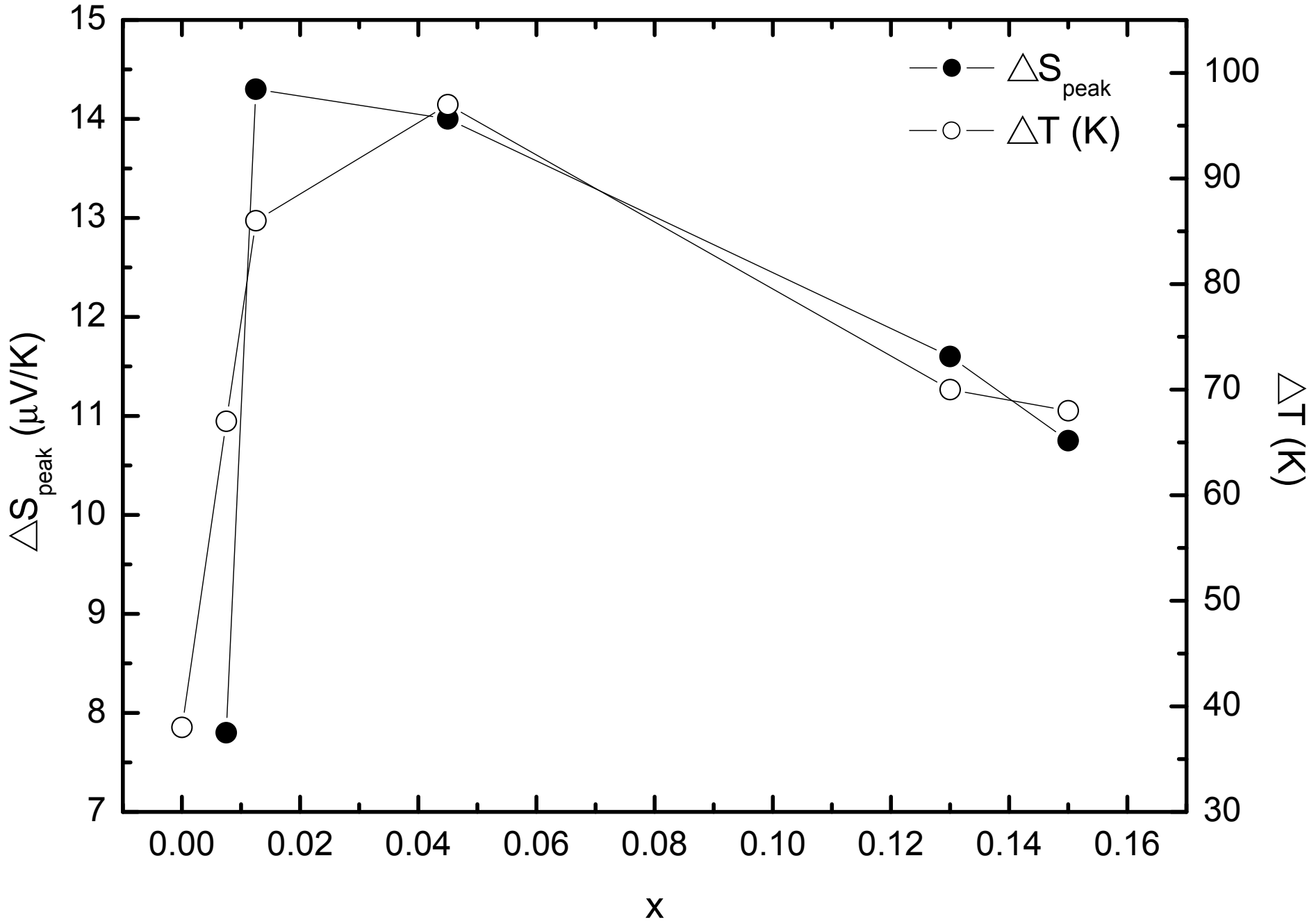
15
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x
△S_peak (μV/K)
△T (K)
△S_peak
△T (K)